



## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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<p>(21) International Application Number: PCT/US98/03656</p> <p>(22) International Filing Date: 25 February 1998 (25.02.98)</p> <p>(30) Priority Data: 60/040,048 7 March 1997 (07.03.97) US</p> <p>(71) Applicant (for all designated States except US): CORNING INCORPORATED [US/US]; 1 Riverfront Plaza, Corning, NY 14831 (US).</p> <p>(72) Inventors; and (75) Inventors/Applicants (for US only): BLACKWELL, Jeffery, L. [US/US]; 289 W. William Street, Corning, NY 14830 (US). DASHER, David [US/US]; 137 Field Street #45, Corning, NY 14830 (US). SUTTON, A., Renee [US/US]; 25 1/2 Earl Street, Corning, NY 14830 (US). TRUESDALE, Carlton, M. [US/US]; 11922 River Road, Corning, NY 14830 (US).</p> <p>(74) Agent: HERZFELD, Alexander, R.; Corning Incorporated, Patent Dept., SP FR 02-12, Corning, NY 14831 (US).</p>		<p>(81) Designated States: JP, KR, US, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).</p> <p><b>Published</b> With international search report.</p>
<p>(54) Title: METHOD OF MAKING TITANIA-DOPED FUSED SILICA</p> <div data-bbox="321 1096 1315 1690"><p>Signal Intensity (arb. units)</p><p>O S T</p></div> <p>Transmission Spectrum of TYZOR DC</p> <p>(57) Abstract</p> <p>This invention relates to production of high purity fused silica glass doped with titania using titanium chelates. Useful chelates include titanium acetylacetonate, and titanium ethyl acetoacetate among others.</p>		

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## METHOD OF MAKING TITANIA-DOPED FUSED SILICA

### FIELD OF THE INVENTION

5           The invention relates generally to the manufacture of high purity metal oxide glass, and specifically to a method of doping high purity fused silica using organotitanium materials.

### BACKGROUND OF THE INVENTION

10           Titania-doped silica glasses have found numerous use in the industry due to its low expansion properties as well as for its excellent resistance to fatigue. In addition, optical fiber having one or more outer layers doped with titania has been shown to exhibit superior strength, as compared to homogeneous silica clad fibers. Superior strength is desirable in optical fiber as it reduces the potential for rupture and  
15 consequential replacement.

          Various methods and apparatus for the production of high purity metal oxides, and particularly fused silica, from a chloride-based feedstock have been well documented. Such equipment generally include a number of burner arrangements and feedstock delivery systems, all based on the oxidation of a metal chloride through flame  
20 hydrolysis or pyrolysis. Illustrative examples are, U.S. Pat. No. 4,491,604 (Lesk et al.) wherein trichlorosilane, dichlorosilane, and silicon tetrachloride are flame hydrolyzed to form soot, and U.S. Pat. No. 3,666,414 (Bayer) wherein silicon halides, such as silicon chloroform, are flame hydrolyzed. In similar processes, U.S. Pat. Nos.

3,486,913 (Zirngibl) and 2,269,059 (McLachlan) teach of oxidation of halides: inorganic halide components in vapor form such as  $\text{TiCl}_4$ ,  $\text{CrCl}_3$ ,  $\text{CrO}_2\text{Cl}_2$ ,  $\text{SiCl}_4$ ,  $\text{AlCl}_3$ ,  $\text{ZrCl}_4$ ,  $\text{FeCl}_2$ ,  $\text{FeCl}_3$ ,  $\text{ZnCl}_2$ , or  $\text{SnCl}_4$  oxidized with air, steam, or oxygen are employed in '913; while silicon halides and  $\text{AlCl}_3$ ,  $\text{TiCl}_4$ , and  $\text{ZrCl}_4$  are employed in '059.

5 U.S. Pat. No. 2,326,059 (Nordberg) details a technique for making silica-rich, ultra-low expansion glass by vaporizing tetrachlorides of Si and Ti into the gas stream of an oxy-gas burner, depositing the resultant mixture to make a preform, vitrifying the preform at  $1500^\circ\text{C}$  to make an opal glass, and firing the opal preform at a higher temperature to cause it to become transparent. Unlike the instant invention, the stated  
10 reference does not employ the use of halide-free, titanium-containing source compounds.

U.S. Pat. No. 4,501,602 (Miller et al.) describes the production of glass and glass/ceramic articles via a vapor phase oxidation process wherein  $\beta$ -diketonate complexes of metals selected from Groups IA, IB, IIA, IIB, IIIA, IIIB, IVA, IVB, and  
15 the rare earth series of the Periodic Table are vaporized, the vapor is transported to an oxidation site, such as a burner or a hot plasma zone which is adjacent to a deposition substrate or within a deposition tube, and oxidized in the vapor phase to form particulate metal oxide soot.

$\beta$ -diketonate complexes are also available of metals in Group VA of the Periodic  
20 Table, notably tantalum and vanadium. Miller et al. did not refer to the halide-free, titanium-containing source compounds employed in the present invention.

Japanese Patent Application No. 90838-1985, entitled MANUFACTURING METHOD OF QUARTZ GLASS PREFORM FOR OPTICAL TRANSMISSION, (Okamoto et al.) discloses a method of doping quartz glass by utilizing an ester silane  
25 expressed by the general formula  $\text{R}^1\text{nSi}(\text{OR}^2)_{4-\text{n}}$  and one or more dopants defined by the formulas  $\text{Ge}(\text{OR}^3)_3$ ,  $\text{B}(\text{OR}^3)_3$  and  $\text{PH}_3$ , where  $\text{R}^1$  is a hydrogen atom, methyl or ethyl group;  $\text{R}^2$  is a methyl or ethyl group;  $\text{R}^3$  is an univalent hydrocarbon group; and n is an integer ranging between 0 and 4. A plethora of organometallic compounds are disclosed including methyltrimethoxysilane, dimethyldimethoxysilane,  
30 trimethylmethoxysilane, tetramethoxysilane, methyltriethoxysilane, and

tetraethoxysilane, though none of the halide-free titania-containing source compounds of the instant invention are mentioned.

Recently, various methods have been suggested for the manufacture of titania-doped silica. For example, co-assigned, U.S. Patent No. 5,067,975, disclosed a method of doping silica with titania using  $\text{SiCl}_4$  and  $\text{TiCl}_4$  for optical fiber applications. The resulting optical fiber includes a core, an inner cladding, and two outer claddings, one nominally about 8% by weight  $\text{TiO}_2$  and a bump layer, with the bump layer having a  $\text{TiO}_2$  concentration greater than 10.5 % by weight. The sole purpose of the bump layer being to control the loss of titania during consolidation.

More recently, co-assigned U.S. Patent No. 5,154,744, disclosed a method of doping silica with titania which method eliminates the need for the bump layer without compromising the strength of the fiber. This patent discloses a method of making titania-doped silica glass having excellent fatigue resistance as well as excellent retention of titania after consolidation, by extracting titania from organometallic compounds selected from titanium tetra isopropoxide, titanium tetra ethoxide, titanium tetra 2-ethylhexyloxyloxy, titanium tetra cyclopentyloxyloxy, and titanium amides.

While the methods disclosed in the above patents have been found adequate for the production of titania-doped fused silica, there continues to be a need for more efficient methods of producing such products. In particular, there is an ongoing need for methods which can be used to produce titania-doped fused silica of improved physical properties.

#### SUMMARY OF THE INVENTION

Briefly, the invention relates to a method of making titania-doped fused silica using a group of organotitanium materials which are less sensitive to air and moisture, and which tend to decompose less than previously disclosed organotitanium materials.

In one aspect, the invention relates to a method of making a non-porous body of high purity fused silica glass doped with titania comprising the steps of:

- (a) forming amorphous particles of high purity fused silica;
- (b) doping said particles with titania in vapor form;
- (c) depositing said titania-doped amorphous particles onto a support; and

(d) either essentially simultaneously with said deposition or subsequent thereto consolidating said deposit of titania-doped amorphous particles into a non-porous body;

the improvement being that the titania is produced using titanium chelates as the titanium-containing compound. Preferred chelates include titanium acetylacetonate, titanium ethyl acetoacetate, and combinations of these.

It is a further object of the instant invention to provide a method of making titania-doped optical fiber having superior strength using as the titania source, the inventive group of organotitanium materials.

#### BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a scanning electron micrograph of the surface layer of a silica blank doped with titania using one of the inventive organotitanium materials; and

FIG.2 is a scanning electron micrograph of the surface layer of silica blank doped with titania using another inventive organotitanium material.

#### DETAILED DESCRIPTION OF THE INVENTION

Most of the processes which have been developed by industry for the manufacture of fused silica such as those used for stepper lens and optical waveguide applications employ the chemical vapor deposition (CVD) concept or a modified version thereof. In a typical CVD process, each of the component liquids (i.e., silica and titania precursor) is heated to a constant temperature at which enough vapor pressure is generated to produce a reasonable rate of deposition. The individual vapors are entrained in a carrier gas stream, mixed together prior to combustion to ensure homogeneous output, and then passed through a burner flame, usually a natural gas/oxygen mixture which frequently contains excess oxygen. The vapors in the mixture are converted to their respective oxides upon exiting the burner orifice to form a stream of volatile gases and finely-divided, amorphous, spherical aggregates, called soot. The soot is collected on a support, for example, on a mandrel (called outside vapor deposition), or on the surface of a bait tube (called axial vapor deposition), and deposited in thin layers of porous preform which is then subjected to high temperatures to consolidate the preform into a non-porous monolithic glassy body.

A two-step process has also been described for the production of doped fused silica. In the first stage, oxygen or nitrogen, the carrier gas, is bubbled through a liquid feedstock of titania and silica precursors. For example, the feedstock may contain titania precursors such as titanium tetra isopropoxide, titanium tetra ethoxide, titanium tetra 2-ethylhexyloxide, titanium tetra cyclopentyloxide, titanium amides and silica precursor such as octamethylcyclotetrasiloxane (OMCTS), maintained at a constant temperature. In one useful embodiment, two feedstock of titania and silica precursors are heated to temperatures in the range of 100-170 °C to generate vaporous reactants. The resulting vaporous reactant are transported to a reaction site, such as a burner, via the carrier gas, wherein the vaporous gas streams are combusted in a burner flame fueled with natural gas and oxygen. The presence of oxygen serves to convert the vaporous reactants to their respective oxides upon exiting the burner orifice to form a stream of volatile gases and finely-divided, spherical particles of soot that are deposited onto a substrate, forming a porous blank, or preform, of opaque, white silica soot. In the second stage, the blank, or preform, is heat treated in a helium/chlorine atmosphere to full consolidation. For optical fiber production, there is a third and final stage in which conventional fiber-draw technology is utilized to pull optical waveguide fiber from the consolidated preform.

In one particularly useful process to which the present invention can be adapted, two raw materials, titania and silica precursors, are separately delivered to a furnace via two tanks. The tanks are maintained at appropriate temperatures to vaporize the raw materials. The vapors are then carried to an udder where they are mixed and burned with oxygen to produce silicon and titania dioxides. In one example, the vapors are carried from the tanks to the udder by flowing a nitrogen gas through the tanks at flow rates appropriate for a given operation. The size of the tanks, as well as the temperature of the raw materials tanks can also vary depending on the vaporization particular raw materials and the desired level of production.

The present method can also be adapted to other fused silica manufacturing processes such as described in U.S. Pat. Nos. 5,043,002, herein incorporated by reference. The inventive process can also be adapted to known methods of producing high purity fused silica by flame pyrolysis or hydrolysis, such as those disclosed in the

early patents by Nordberg (U.S. Pat. No. 2,239,551) in 1941 and Hyde (U.S. Patent No. 2,272,342) in 1942.

It has been observed that during consolidation of porous preforms of silica, the chlorine in the consolidation atmosphere may remove OH from the glass thereby limiting the optical transmission of the resulting glass. Therefore, such compounds must be compatible with the organosilicon compound. By "compatible" it is meant that such organotitanium compound must not self-polymerize or polymerize with the organometallic precursors of silica. In addition to ease of production of titania soot, it is also important that the organotitanium compound exhibit both thermal and moisture stability.

We have found that particularly in the two-step process described above, conventional organotitanium precursors such as titanium tetra isopropoxide and other similar precursors are sensitive to air and moisture and tend to decompose with prolonged exposure to high temperatures typical of such processes. Thus, in applications utilizing such material, it is generally necessary to keep moisture away from the material, for example, by placing the material in an environment having a positive nitrogen pressure in order to prevent the accumulation of water vapor in the air. In addition, titanium tetra isopropoxide tends to hydrolyze in the presence of water making it inefficient as a source of titania.

We have also found that while conventional organotitanium materials such as titanium (tetra) isopropoxide may be useful in processes where the production of the silica and titania gas streams employ a vaporizer, these conventional titania precursors are not as efficient in processes which do not employ vaporizers. This is particularly true in processes which utilize bubblers because in such processes the precursors are subjected to high temperatures for extended periods of time. Such extended high temperature exposure in some cases leads to decolorization and/or decomposition of the precursor and may result in such quality problems as seeds and inclusions being formed in the glass. Other problems which may result includes clogging up of the apparatus which then lead to costly clean ups and high manufacturing cost. Most significantly, conventional organotitanium materials yield low titania soot deposits. In contrast, we



have found that the above problems are significantly reduced if not eliminated by the use of the organotitanium materials described below.

We have discovered a group of organotitanium materials, titanium chelates, which are compatible with OMCTS, less sensitive to air and moisture, and which tend to decompose less than titanium isopropoxide. By compatible, we mean that the titanium chelate does not polymerize itself or with the silica precursor as polymerization leads to a decrease in the vapor pressure, and in the absence of vaporization the result is a decrease in the amount of titania soot collected. Any titanium chelate which is compatible with the silicon precursor, is relatively insensitive to both air and moisture, and which will not prematurely decompose or polymerize, may be used in the present method. Conventional organotitanium materials such as titanium isopropoxide have a tendency to prematurely breakdown (decompose) before the end of the processing period (less than 7 days and in some cases, less than 4 days). The ideal processing time is about 6 to 7 days, preferably, 160 hours. We have found that the inventive chelate materials are able to withstand the operating temperatures for prolonged periods of time and as such do not show the premature decompositions observed in conventional alkoxide materials. Preferred titanium chelates are those having a boiling point of 250 °C or less. We have found one class of titanium chelates, the amines, and in particular titanium diethanolamine to be incompatible with siloxanes, in particular, OMCTS. Other titanium chelates which are not useful for the present invention include titanium di(dioctylpyrophosphate) oxyacetate, titanium di(butyl, octylpyrophosphate) di(dioctyl, hydrogen phosphite) oxyacetate. These compounds exhibit low volatility and are unacceptable because they are likely to introduce phosphorous into the glass. Another compound which is not particularly preferred is titanium tetra acetate, a low volatility solid.

Examples of useful titanium chelates include, titanium acetylacetonates, and titanium ethyl acetoacetates in particular bis(ethylacetoacetato) diisopropoxy titanate (TYZOR® DC) and acetylacetonate titanate chelate (TYZOR® GBA) both available from DuPont, Wilmington, Delaware. In addition to being compatible with OMCTS, these chelates are also generally miscible with the silica precursors.

## EXAMPLES

In the following examples, we demonstrate the production of titania soot using the inventive titanium precursors. Two preferred titanium chelates, titanium acetylacetonate (GBA), and titanium ethyl acetoacetate (DC) were used to produce titania soot using a chemical vapor deposition (CVD) method under the following conditions:

Premix CH <sub>4</sub> (lpm)	4.0
Premix O <sub>2</sub> (lpm)	3.6
Inner shield O <sub>2</sub> (lpm)	2.0
Outer shield O <sub>2</sub> (lpm)	6.3
Carrier N <sub>2</sub> (lpm)	2.5
Vaporizer Temp. (°C)	230
Vaporizer fume Temp. (°C)	215
Delivery Rate (g.min)	2.0

For comparison, a third precursor, titanium diethanolamine - (TYZOR<sup>®</sup> DEA) was used under the above conditions except that lower vaporizer and fume temperatures were used, namely, 120 and 100 °C respectively. At this condition no titania soot was observed or collected on the slide. The vaporizer temperature was raised to 230 °C and at this temperature, only very little amount of soot was collected on a slide.

The results from the DC and GBA precursors are shown in FIGS. 1 and 2, and as Examples 1 and 2 respectively in the following table. Titanium tetra isopropoxide (Ti-POX) precursor is shown for comparison (C-1).

Example	Precursor	Boiling Point (°C)	Viscosity (cPoise)	( <sup>1</sup> ) (%Ti)	Performance
C-1	Ti-POX	232	3	17	Hydrolyzes Compatible
1	GBA	70	6	10	Stable, Moisture and air insensitive, some phase

separation

2	DC	220	37	11	Very stable, air and moisture
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5 insensitive,  
compatible

<sup>(1)</sup> Concentration of titanium in the organotitanium precursor.

As shown, the titanium chelates produced titania soot which exhibited very good physical and performance properties. An analysis of the soot using transmission microscopy showed that these organotitanium compounds produced acceptably high performance (measured by the intensity of  $\text{TiO}_2$  to  $\text{SiO}_2$ .) These results are shown in FIGS. 1 and 2.

Example 2, using DC represents the most preferred embodiment of the  
15 invention both in terms of stability and soot production.

## CLAIMS:

1. In a method for making a body of high purity fused silica glass doped with titania comprising the steps of:

- (a) forming amorphous particles of high purity fused silica;
- (b) doping said particles with titania in vapor form; and
- (c) depositing said titania-doped amorphous particles onto a support;

the improvement being that said titania is produced from titanium-containing compound selected from the group consisting of titanium acetylacetonate, titanium ethyl acetoacetate, and combinations thereof.

2. The method according to claim 1, further comprising the step of either essentially simultaneously with said deposition or subsequent thereto consolidating said deposit of titania-doped amorphous particles into a non-porous body.

3. The method according to claim 2, wherein said titania-doped amorphous particles are characterized by having submicroscopic crystals of rutile and anatase with rutile being the predominant crystal phase.

4. The method according to claim 1, wherein said titanium-containing compound is halide-free.

5. The method of claim 2, wherein the non-porous body is an optical fiber.

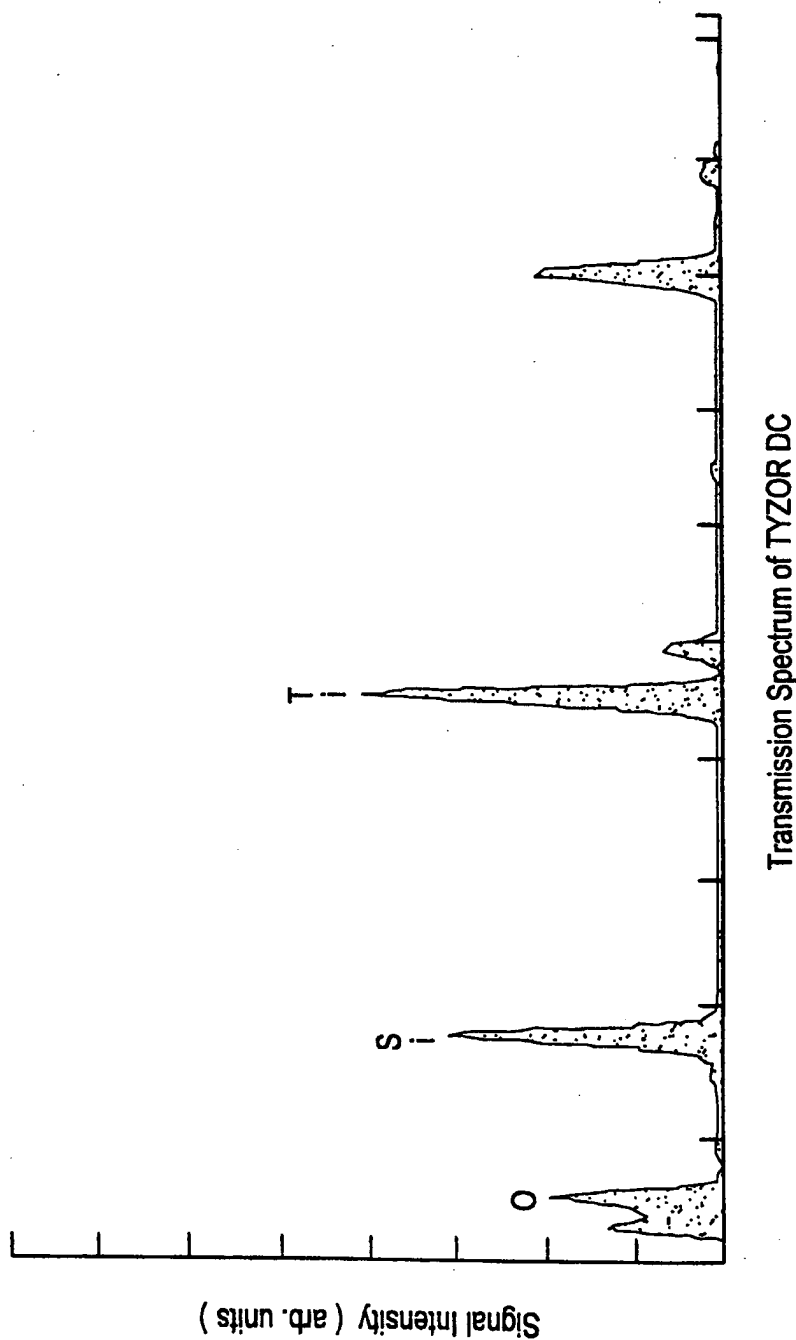
6. The method of claim 4, wherein the support is selected from the group consisting of a mandrel, and a bait tube.

7. The method of claim 2, further comprising the step of drawing the consolidated non-porous body to form a waveguide fiber.]

8. Fused silica made by the method according to claims 1 to 4.

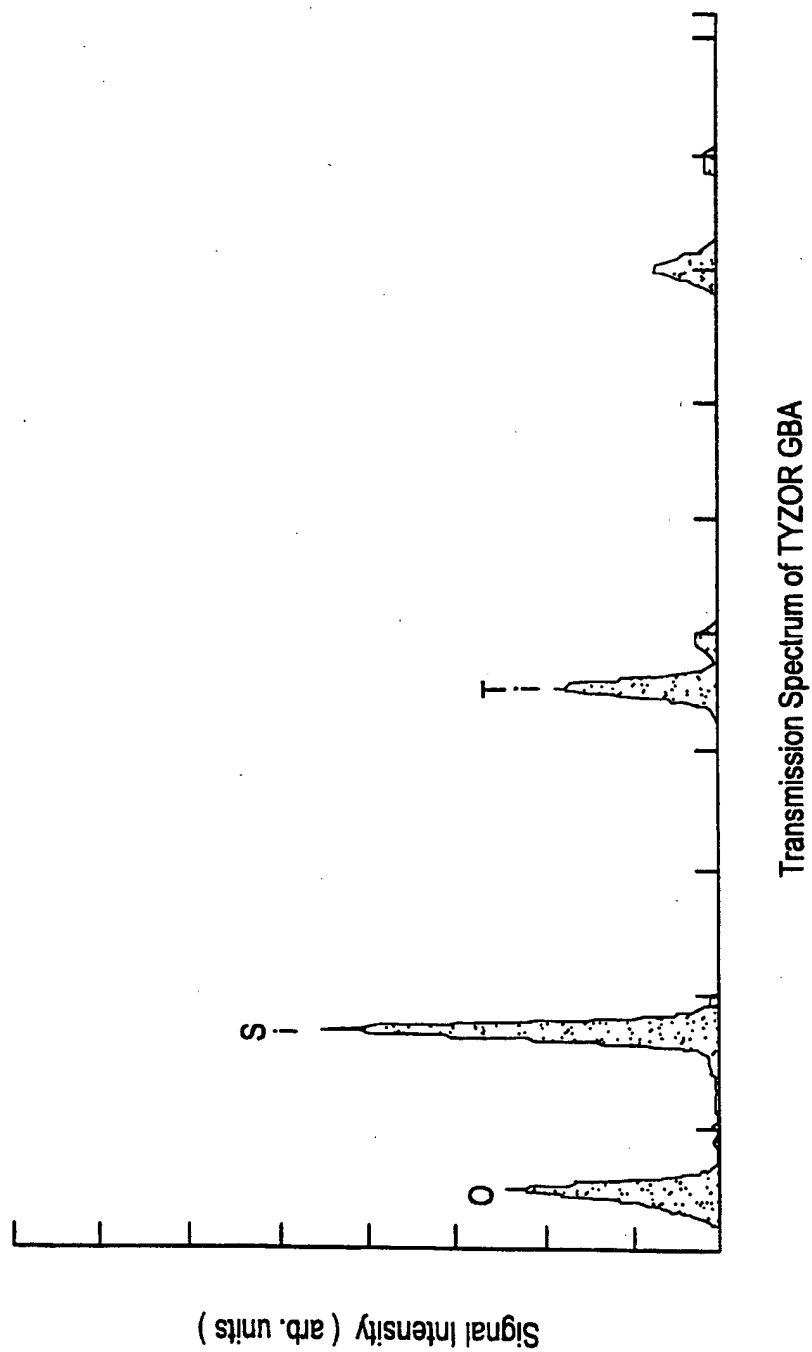
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FIG. 1



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FIG. 2



## INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US98/03656

**A. CLASSIFICATION OF SUBJECT MATTER**

IPC(6) :C23C 16/40; B29D 11/00

US CL :Please See Extra Sheet.

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 427/163, 163.2, 166, 167, 452, 453, 255.2, 255.3, 255; 423/326, 336, 337, 610, 598; 264/1.24, 1.28, 81; 65/413

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

APS; STN

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 5,154,744 A (BLACKWELL et al.) 13 October 1992 (13-10-92), column 1, lines 53-68; column 2, lines 60-68; column 4, lines 34-55; column 5, lines 2-7 and 25-43.	1-7
Y	Lee et al., Preparation and Characterization of Titanium(IV) Oxide Photocatalysts, Materials Research Bulletin, June 1992, Vol. 27, No. 6, pp. 685-692, especially p. 686.	1-7

☐ Further documents are listed in the continuation of Box C.☐ See patent family annex.

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\*Y\*

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document member of the same patent family

Date of the actual completion of the international search

14 MAY 1998

Date of mailing of the international search report

09 JUN 1998

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INTERNATIONAL SEARCH REPORT

International application No.  
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A. CLASSIFICATION OF SUBJECT MATTER:  
US CL :

427/163, 163.2, 166, 167, 452, 453, 255.2, 255.3, 255; 423/326, 336, 337, 610, 598; 264/1.24, 1.28, 81; 65/413



# INTERNATIONAL SEARCH REPORT

International application No.  
PCT/JS98/03656

## Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This international report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:  
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:  
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
3. ☒ Claims Nos.: 8  
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

## Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.  
☐ No protest accompanied the payment of additional search fees.